IIMT UNIVERSITY, MEERUT

SYNOPSIS

Submitted

In partial fulfillment for the award of
the Degree of Doctor of Philosophy

On the Topic

"Bio remediation of heavy metals from soil and water bodies: A comparative experimental study for the effectiveness of phyto remediation through different methods :An effective tool for minimizing the heavy metal contamination in agricultural soil and water bodies in rural region of Meerut U.P."

(MANMOHAN VERMA)

Department of Basic Science, Department of chemistry
(June 2021)

Introduction:

Heavy metals are cause for several diseases like- Wilson's menkens, alzheimer's , parkinson's, itai-itai, nervour system disoeder, kidney disorder, liver disorder, heart dis order/failure etc. A data show that about 20 million ha of land in more than 5 million sites have different type of heavy metal contamination in the world.
In phytoremediation process hyperaccumulation and good tolerance are more necessary than high biomass[7].

Heavy metal contamination of soil and water bodies is very leading source of pollution and serious menace for human health, animal health and aquatic ecosystem. Other technologies used to remove heavy metal pollutants from water body or from soil are time consuming, very costly, harmful to environment and not feasible and create secondary pollution etc. While phytoremediation techniques are used to remove inorganic and organic pollutants. Phytoremediation technique is of low cost, time saving , eco- friendly, environment friendly and easy to perform experiments. Already there is very scarcity of drinkable water in the world as well in India, then heavy metal pollution in water sources like ponds, underground water, river, drains create a very dangerous situation for fauna and flora.

Various metals are needed in our daily developmental activities like growing food requirement, growing number of small and big industries, growing population, growing consumption, growing house hold and industrial wastes, fast urbanization, growing use of pesticides, insecticides and fertilizers in agriculture leads soil and water contamination.

Industries like – geothermal energy plants, sugar industry, paint industry, color-paper industry, (Cr, Hg, Pb, As,Sb, Sn, Ni etc) metal extraction industry, metal related industry, pesticide industry, herbicide industry, soap industry, Dyeing industries, automobile, tanning industry, mining, plastic industries, rubber industry, battery and cell mfg industry, hazardous chemical industries etc create point sources for water and soil pollution. To fulfill the increasing demand of above industries and households, reclamation of contaminated water is the only option and solution. Heavy metals in soil and water are non biodegradable and exist in the soil and water bodies for hundreds of years. Toxic heavy metals come in water and soil from different industries and from domestic/ household wastes. These contaminants from water go in food products from soils. Heavy metals accumulate with time and do not corrode. Heavy metal removal is very complicated because they exist in various oxidation states. There are several techniques which are used in to remove

heavy metals from contaminated water. These techniques are chemical precipitation, extraction by solvents, ion exchange method, reverse osmosis, adsorption and evaporation of water etc. But these techniques involves high number of operations, time consuming and very high cost of each project thus these techniques become practically impossible. Thus phytoremediation is very versatile techniques which purify contaminated water and soil comparatively fast and economical. Aquatic plants and some other plants have high potential to remove heavy metals from contaminated water [1].

Many research have shown that a number of plants can increase biological degradation of harmful organic molecules in soil [2]. Toxic heavy metals naturally present in the soil and water , but when they accumulate in more than prescribed limit these heavy metals become destructive pollutants [2].

There are different phytoremediation techniques like—phytoextraction, phytovolatization, phytodegradation, phytostbilization, rhizofiltration, rhidegradation and phytodesaqlination. Different plants do phytoremediation in different way and in different efficieancy.

Table -1 : heavy metal source and its adverse effect [3].

Heavy metals/level	**Sources**	**Adverse effect**
High poisonous		
Hg	Coal burning , medical waste and mining	Neurotoxin it damage brain function, lung, kidney
As	Herbicides, pesticides, cosmetics, paints, anti spasm, anti analgesic	Cell damage, carcinogenic
Se	Paint , glass, metallurgy, electronics, pharmaceutic.	Respiratory problem, cardiovascular disease, hypertension.
Cd	Pigments, metallurgy, battery, electroplating, insecticides, solder, , textiles.	It affect nutrient reabsorption and Damage to renal tubules,
Pb	Fertilizer, pesticides, insecticides, pigments, gasoline, smelting of ore.	Badly affect kidney, heart, brain and lungs.
Zn	House & Official hardware, galvanization of more	Kidney and liver failure, stomach ach, epigastric pain, diarrhea, blood in urine.

	reactive metals, Alooys, heating conducts.	
Cu poisonous	Electric wires, battery, water pipes, fungicides, insecticides, metallurgy, pigments.	G astrointestinal bleeding, diarrhea, epigastric pain, hemolytic anemia.
Cr	Refractory, electroplating, Leather tanning, Metallurgy	Allergic skin inflammation, dermatitis, Ulcerations.
Ni	Smelting, industrial waste, municipal waste, steel and cement industry, Mining, vehicle emission.	Emphysema, Lung inflammation.

Table-2: Different water and soil plants which are used to remove specific heavy metals. **[1, 9, 10]**.

S. No	Aquatic and soil plants	Common Name	Metals/Metalloids
1	Eichhornia crassipes	Water hyacinth	Pb, Hg, Cu Cr, Ni, Zn
2	Pistia stratiotes	Water lettuce	Cr, Zn Fe, Mn, Cu
3	Salvinia minima	Water spangles	As, Ni Cr, Cd
4	Salvinia herzoggii	Water fern	Cd, Cr
5	Lemna minor	Duckweed	Cr, As, Ni, Cu, Pb
6	Spirodela intermedia	Duckweed	Fe, Zn, Mn, Cu, Cr, Pb
7	Nasturtium officinale	Water cress	Cr, Ni Zn, Cu
8	Myriophyllum spicatum	Parrot feathers	Pb, Cd, Fe Cu
9	Ceratophyllum demersum	Hornwort	As, Cd, Cr,Pb
10	Potamogeton crispus	Pondweed	Cu, Fe, Ni, Zn, Mn
11	Potamogeton pectinatus	American pondweed	Cd, Pb, Cu Zn
12	Typha latifolia	Common cattail	Zn, Mn, Ni, Fe, Pb, Cu
13	Mentha aquatica	Water mint	Pb, Cd, Fe, Cu

14	Vallisneria spiralis	Tape grass	As
15	Spartina alterniflora	Cordgrass	Cu, Cr, Zn, Ni, Mn, Cd Pb, As
16	Phragmites australis	Common reed	Fe, Cu, Cd, Pb, Zn
17	Scirpus	Bulrush	Cd, Fe, Al
18	Polygonum hydropiperoides	Smartweed	Cu, Pb, Zn
19	Brassica juncea	Indian mustard	Pb, Cd, Zn

Plants absorb ionic compounds even at low concentration by their roots . plants expand their roots in the soil and create rhizosphere ecosystem which accumulate heavy metal ions. Phytoremediation method is a autotrophic which get energy from solar radiation. It is simple to establish and manage. Maintenance cost is low. This method can be applied over a big field or land. This method stop erosion of soil. This method increase soil fertility with a number of organic compost manure [4].

Literature Review:

Water hyacinth (Eichhornia crassipes), water lettuce (Pistia stratiotes) and Duck weed (Lemna minor) along with some other aquatic plants are prominent heavy metal accumulator. Xenobiotic organic molecules like-pesticides, herbicides, hydrocarbons accumulate in the soil and water. Collection rates of these xenobiotics pollutants in the soil and water are more than their removal [2]. In biodegradation, xenobiotic bacteria and other microorganism convert exogenous organic molecules in to fatty acides, alcohols or CO_2 etc. 1-Oats roots biodegrade phenanthrene . Festuca arundinacea L and panicum virgatum L biodegrade pyrene[2] . In biodegradation microorganism receive their nutritional and energy demand for its growth and thus detoxify environment [2].

Toxic heavy metals are referred as environment pollutants. Non metals –As, Se, and Sb are also considered environment pollutants. Heavy metals can be divided in biologically essential and non essential metals. Although boundary of this division is not clear. The biologically essential metals are Fe, Mn, Zn, Cu,Co, Mo while Ni and Cr are less important metals. The biologically non essential metals are Cd, Hg, Pb, As. Heavy metals either biologically essential or non essential will become toxic

when they present in more than a limit in the body. Because they negatively affect our health. Heavy metals can be transferred to human through food, water, skin and dust. Metamorphic and Igneous rocks present on the surface of the earth is about 95%. These rocks discharge continuously Mn, Ni, Cu, Co, Zn and Cr heavy metals in the soil. Rocks at different places may have different kind of metals and different amount of heavy metals [2].

The heavy metals like-Pb, Hg, Cu, Cr, Cd, Zn, Mo with some metalloids As sb, Se etc released from industrial works are about 10 to 20 times more than the amount of heavy metals released by weathering of rocks [2].

Contaminated soils may be converted in to normal soil but it is much costly and pollution problems do not get solved also. Chemical techniques of heavy metal remediation will produce another type of pollution problems. In phytoremediation techniques plants and soil microbes are used to remove pollutants in water and soil. Heavy metals presents in the soil in the form of metal complexes, ions, carbonates, sulphates, phosphates, nitrates, hydroxides, oxides, halides and in silicate chains. Heavy metals affect adversely our health and eco system. Our development in such condition can not said as sustainable development.

In thermal desorption method, soil is treated at high temperature (between 320 to 560^{O}C and 90 to 329^{O}C) with steam, infrared radiation, carrier gas separation, vacuum and microwave etc and volatile heavy metals (Hg, As) are removed. But this technique is time consuming and very costly. Another remediation technique is washing / chemical leaching. In this technique, freshwater, chelating agents and solvents are used to wash soil. Heavy metals are removed from soil to liquid solvent and leachate. Leachate has surfactants, heavy metals and chelating agents. This technique is highly expensive and time consuming. Another method of soil remediation is elctrokinetic method, in this method two electrodes are inserted in the soil and low electric field is generated. Here electro osmosis, electrophoresis and electro migration are deriving forces to transfer heavy metal ion to electrodes where heavy metals get precipitated. This method is easy and of low cost , but it change the pH value in the soil. Electric flow may be diverted to buried metal piece in soil thus it requires longer time in the process. Any soil remediation method which does not damage the natural ecosystem of the soil is termed as environment friendly method [3].

Heavy metals pollution in agriculture soil affects badly our ecosystem, human life and wild life. Phytoremediation method is cheap, environment friendly , eco

friendly, easy to perform and time saving as well. Phytoremediation is the best method to settle the problems of heavy metals. Phytoremediation term came in 1991 from Phyto plant] and remediation [recovery] words. In this method plants are used to remove inorganic and organic contaminants from polluted area. It does not require any special equipment during the process. PH level of the soil area should be between 5.8 to 6.5 so that heavy metals can be absorbed by the plants.

Theories which explain the transport of nutrients to the root surface are contact change / intersection and carbonic acid theory [4].

These heavy metals enter in food chain through plant products and accumulate in the human, animals, birds body through biomagnifications and become threat to their health. Mostly heavy metal are not available to plants. Because plants release various root exudates, this change rhizosphere pH and increase solubility of heavy metals. Heavy metals get sorbed on root surface and cross root membrane then go to root cells. There are two pathway of heavy metal absorption in roots. 1-apoplastic path/ passive diffusion and symplastic path/ active transport with respect to electrochemical potential difference and concentration difference across the plasma membrane. When heavy metal ions enter into root cells, they form complex chelates like- with organic acids. These complexes also have carbonate, phosphate or sulphates, which stay in intracellular area{ symplastic part as vacuoles}/ extracellular space {apoplastic cellular walls} as well. Heavy metal ions sequestered (separate/remove) in vacuoles transport into stele then they enter in the xylem vessels where from they go to shoots and in the last to leaves [5].

Transporter of heavy metal ion:

The heavy metals transporters are channel proteins/ H-coupled carrier proteins. which present in the plasma membrane of root cells . Thus heavy metals are transported through cellular membranes of cells. These transporters mediate efflux and influx of heavy metal ions from roots to shoots. In sequence homology, families of metal transporters are ZIP, NRAMPs, MTPS and HMAs. ZIP (ZRT-IRT-proteins) family transporters are hyperaccumulator (thlaspi caerulescens and Arabidopsis halleri) for Zn and Fe,Mn. P1B-type-ATPases (HMAs) is also transporter family and transport Zn, Cd, Pb,Co , which help in homeostasis/ tolerance. Transporter proteins family MTPs translocate-Zn and Ni . Resistance associated macrophage proteins (NRAMPs) translocate-Fe, Cd, Co, Mn and Cu. There are some complex forming agents like-organic acids, amino acids, citrate, histidine etc which acts as metal ligands to facilitate chelation of heavy metal ions. Citrate is main chelating agent for Ni and Fe in the xylem [5].

Mechanism of detoxification:

Detoxification is requirement in phytoremediation process. Plants use two defense mechanism to cope with the toxicity of heavy metals. These defense mechanisms are tolerance and avoidance [5].

[a] **Avoidance:** In this mechanism , plants restrict the heavy metal uptake.

Plants first immobilize ions as root sorption, modifying ions and by making chelate complexes in rhizosphere area. Various root exudates may change pH of rhizosphere thus making heavy metal ions ommibilise . These processes limit the bioavailability of heavy metal ions to the plants [5].

[b] Tolerfance: It is second defense mechanism of plants at intracellular level. When heavy metal ions enter in cytosol, plants use chelation, inactivation and immobilization / restriction of heavy metal ions. Excess heavy metal ions in the cytosol are entrapped by making chelates thus toxicity of them are reduced to low level. Some organic chelating agent are amino acids. organic acids, metallothioneins, phyto chelatins and cell wall proteins/polyphenols etc.

Citrate mediates chelation with Ni in T. goesingense leaves. Citric/acetic acids make chelate with Cd in solanum nigrum leaves. Malate make chelate with Zn in A. halleri. Excess Ni induce histidine accumulation while excess Zn, Pb, Cu and Cd induce proline. Heavy metals are immobilized and detoxified by making chelates with amino acides in cells and in xylem sap. These complexes are transported from cytosol to inactive vacuole after chelation [5].

The primary heavy metal accumulators are discussed below. Brassica juncea(Indian mustard) , Radish and Kale can accumulate several heavy metals. Lead(Pb) is absorbed in their roots(mainly), shoots and fruits from the soil effectively and EDTA increase Pb accumulation . Brassicaceae is a angiosperm group. It grow in high temperature region and have genera such as Sinapis, Camelina, Thlapsi, Brassica and Crambe. The gener Brassica include crops as Brassica napus L, Brassica oleracea L, Brassica rapa L(turnip), Brassica juncea (brown mustard) and Brassica nigra (black mustard). Brassica oleracea include kohlrabi, Brussels sprouts, broccoli, cauliflower, cabbage, kale etc.
Some chelating agentgs such as N-(2-hydroxyethyl)-ethylenediamine triacetic acid[HEDTA], EDTA and acetic acid etc are used to increase mobility of heavy metals(Pb, Cu,Zn) thus increasing phytoextraction. Copper is accumulated by Brassica juncea through roots, fruits (mainly) and by shoots (less amount). Here EDTA increase the accumulation of Cu. Zinc is accumulated by Brassica juncea through shoots (mainly) and by roots (less amount). Here EDTA has no effect on the accumulation of Zn [7].

Chromium(III) is essential in traces in diet to regulate the glucose metabolism in the body. But excess of it is carcinogenic. Plants which are used in phytoremediation in chromium case are para grass(brachiara mutica), swamp smartweed(polygonum coocineum) and papyrus(Cyprus papyrus). In a compsarative study of phytoremediation, Cr-III in synthetic chromium polluted soil and in tannery polluted soil experiments were determined by ICP-OES. Cr –III was significantly accumulated in roots and shoots of para grass and papyrus is relatively high [8].

Objective of the work and hypotheses:

1. Analysis of soil & water sample contaminated by heavy metals in rural region of Meerut U.P.
2. Analyis of the presence of types of heavy metals likely to found in the specific area of Meerut U.P. region.
3. Identification of Phytoplanktons & plants found to grow in the region & found effective for bioremediation.
4. Identification of methods for phytoremediation & a comparative study for the effectiveness of different methods for the purpose.

Methodology of your work plan:

The methodology will be divided into following two categories-

i. Chemical techniques

ii. Bioremediation by growing specific plants in contaminated water bodies & on contaminated soil based on their effectiveness for a particular heavy metal removal.

References:

1- Application of Floating Aquatic Plants in Phytoremediation of Heavy Metals Polluted Water: A Review, Sustainaqbility [MDPI] , Received: 11 February 2020; Accepted: 24 February 2020; Published: 3 March 2020.

2-Prieto Méndez J, Acevedo Sandoval OA, Prieto García F, Nallely Trejo González, Phytoremediation of soils contaminated with heavy metals. Received: July 19, 2018 | Published: August 9, 2018.

3- Removal of Heavy Metals in Contaminated Soil by Phytoremediation Mechanism: a Review, Soo Hui Awa & Tony Hadibarata, Received: 27 November

2019 /Accepted: 17 January 2020/ published online : 21 january 2020. Springer Nature Switzerland AG 2020.

4- Sevinc Adiloglu. Book- Heavy metals removal with phytoremediation. Submitted: 23-february 2017, Reviewed:6-july 2017 , published 20-december 2017, DOI: 10.5772/intechopen 70330.
https://www.intechopen.com/books/advances-in-bioremediation-and-phytoremediation/heavy-metal-removal-with-phytoremediation.

5- An Yan, Yamin Wang, Swee Ngin Tan, Mohmed Lokman, Mohd Yusof, Subhadip Ghosh and Zhong Chen. Phytoremediation: A Promising Approach for Revegetation of Heavy Metal-Polluted Land. Frontiers plant Science, Vol-11, 2020.

6- Georgiana Luiza Arnold Tatu, Nicolae Valentin Vladut, Iulian Voicea, Nicoleta Alexandra Vanghele, and Mirabela Augustina Pruteanu*, Removal of heavy metals from a contaminated soil using phytoremediation, MATEC Web of Conferences 305, 00061 (2020) SESAM 2019, https:// doi.org/10.1051 /matecconf/ 202030500061

7- Gemechu Kassaye, Nigus Gabbive, Agegnehu Alemu. Phytoremediation of chromium from tannery wastewater using local plant species. Water Practice and Technology (2017) 12 (4): 894–901.
https://doi.org/10.2166/wpt.2017.094.
https://iwaponline.com/wpt/article/12/4/894/38660/Phytoremediation-of-chromium-from-tannery-.

8-Ali, E. K. & Sajad M. A.2013, Phytoremediation of heavy metals concepts and applications *Chemosphere*, 91 (7), 869–881.

9-Abhijit Mitra, university of Calcutta, India. Phytoremediation by mustard plant, Sept-2017.

10-8-P.K.Gautam, R.K.Gautam, S. Banerjeet, M.C.Chattopadhyaya, J.D.Pandey, Chemistry department, University of Allahabad, India. Heavy metals in the environment: fate, transport, toxicity and remediation technologies. Nova science publishers, capter-4, p101-130, ResearchGate-February 2016.